Electronic Supplementary Information (ESI)

for

Luminescent Zn(II)-terpyridine metal-organic gel for visual recognition of anions

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Materials and Methods: All reagents were purchased commercially and used without further purification. The ligand 4-[2,2':6',2"-terpyridin]-4'-ylbenzoic acid (Hcptpy) (97%) were obtained from Shanghai UCHEN Inc. The morphology of the metal-organic gels (MOGs) was characterized by an S-4800 scanning electron microscope (SEM) (Hitachi, Japan). Powder X-ray diffraction (XPRD) patterns were collected on a XD-3 X-ray diffractometer with Cu Ka radiation (λ=1.5406 Å) in the range of 5-80 2-θ at a scan rate of 2.00 min^{-1} (Purkinje, China). Elemental analysis was performed on a Carlo-Erba-1106 instrument. FTIR spectra were recorded on a FITI-8400 (Shimadzu, Japan) in the range of 4000-500 cm^{-1} using the KBr disk method at RT. The thermal properties of the supramolecular gels were measured on a DSC-Q200 at a scan rate of 10 $^oC\ min^{-1}$ under N_2 atmosphere. The fluorescence measurements were made on an F-2500 spectrofluorimeter (Hitatch, Tokyo, Japan). The solid fluorescence absolute quantum yields were measured on a C11347 absolute pl quantum yield spectrometer (Hananatsu, Japan). The xerogels were obtained by a Coolsafe 110-4 freeze-drying apparatus (Labogene, Denmark).

Gel Preparation: In a typical gel formation reaction, Hcptpy (5 mg, 0.014 mmol) was added in the $ZnSO_4 \cdot 7H_2O$ aqueous solution (1 mL, 0.024 moL). After added 2 μL TEA in the mixture solution, the solution was rapidly mixed. Then the homogeneous solution was left to stand at 80^{o}C for 10 min in a water bath. An opaque wet gel was obtained.

Sample preparation: The MOGs which prepared according to above methods have been interacted with 200 μL 0.2 M different anions beyond 1 hour for full reactions. These MOGs were transformed to xerogels by vacuum freeze-drying method for XRD analysis. In addition, the samples for SEM were prepared by dropping a little product onto the silicon slices and dried under 30^{o}C for 5 hours in vacuum condition.

Additional Figures:

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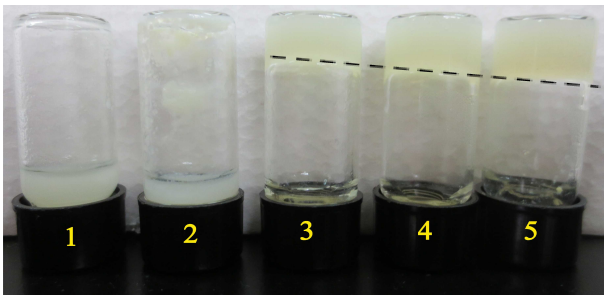


Fig. S1 Gelation tests of Zn(II)-Hcptpy with different temperature. T(^{o}C ,1-5): 25, 30, 40, 60, 80.

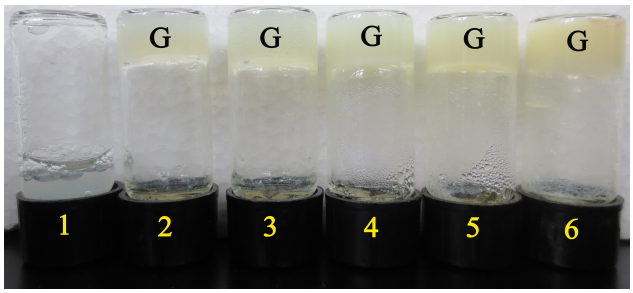


Fig. S2 Gelation tests of Zn(II)-Hcptpy with different mass of Hcptpy. c_{Hcptpy}(μM, 1-6):2.8, 5.6, 11.2, 16.9, 22.6, 28.2.

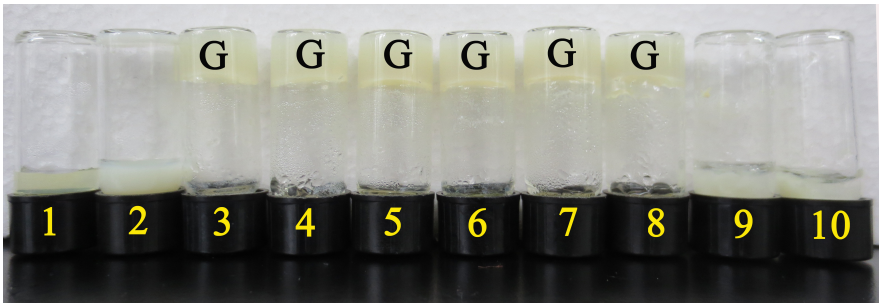


Fig. S3 Gelation tests of Zn(II)-Hcptpy with different concentration of Zn^{2+}. $c_{Zn}{}^{2+}$(μM, 1-10),0,6,12,18,24,30,60,90,120,150.

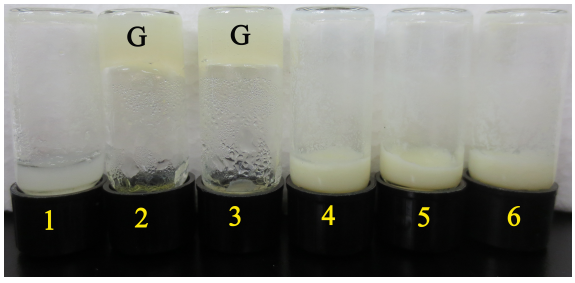


Fig. S4 Gelation tests of Zn(II)-Hcptpy with different amount of TEA. V_{TEA}(μL ,1-6) 0, 2, 4, 6, 8, 10.

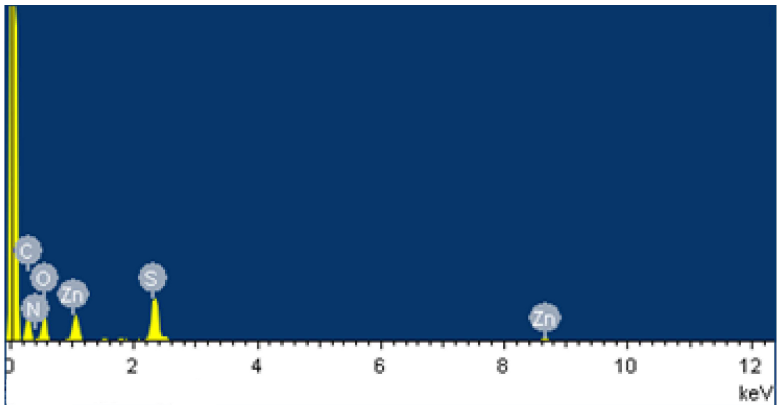


Fig. S5 EDS spectrum of the xerogels.

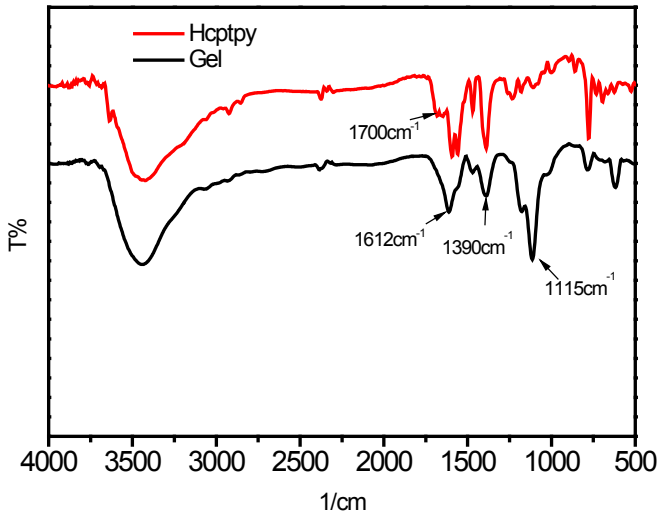
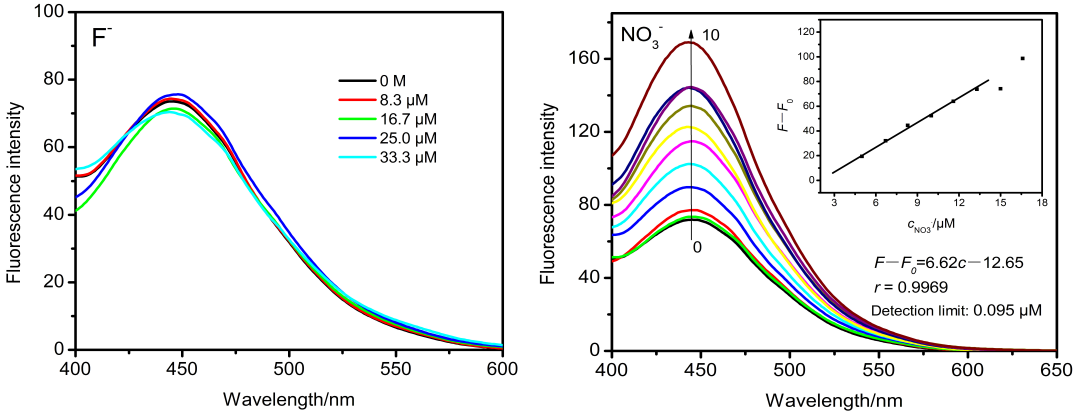


Fig. S6 Fourier-transform infrared (FTIR) spectrum of the Hcptpy and xerogels.



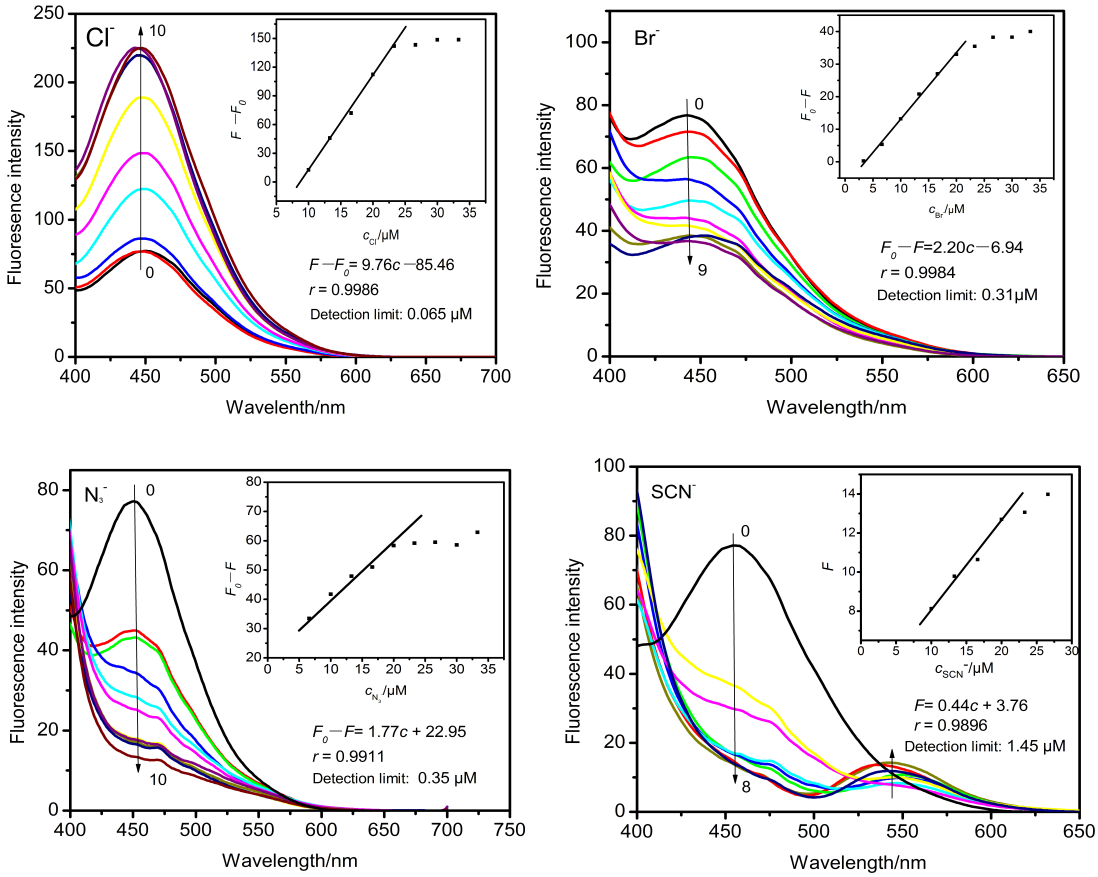


Fig. S7 The fluorescence spectra of MOGs upon addition of different concentration of anions (inset calibration curve in NO_3^-, Cl^-, Br^- and N_3^- is the relative intensity of fluorescence versus different concentrations of anions; inset calibration curve in SCN^- is the fluorescence intensity at ~ 550 nm versus different concentration of SCN^-). c(Cl^-, Br^-, N_3^-, SCN^-, μM, curves 0-10), 0, 3.3, 6.6, 10, 13.3, 16.6, 20, 23.3, 26.6, 30, 33.3, respectively; c_{NO3}^-(μM, curves 0-10), 0, 1.67, 3.3, 5, 6.7, 8.4, 10, 11.6, 13.3, 15, 16.6, respectively.

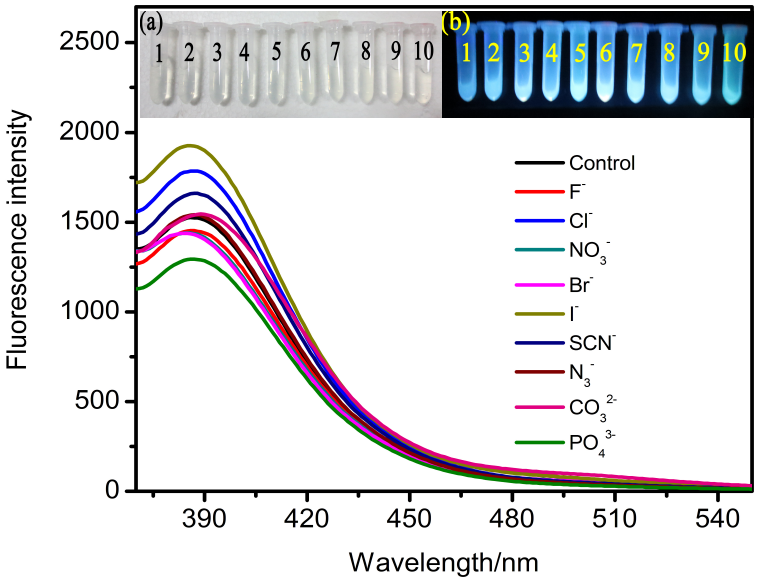


Fig. S8 Fluorescence emission spectra of the MOGs mixture without the zinc ions (Hcptpy and TEA solutions) in the absence and presence of anions; λ_{ex}= 350 nm; voltage = 400 V; The concentration of the anions is 0.03 M, respectively. Insets are the photographs of these solutions under daylight (a) and under 365 nm UV light (b); From 1 to 10 is control (Hcptpy+TEA), control + F^-, control + Cl^-, control + NO_3^-, control + Br^-, control + I^-, control + SCN^-, control + N_3^-, control + CO_3^{2-}, control + PO_4^{3-}, respectively.

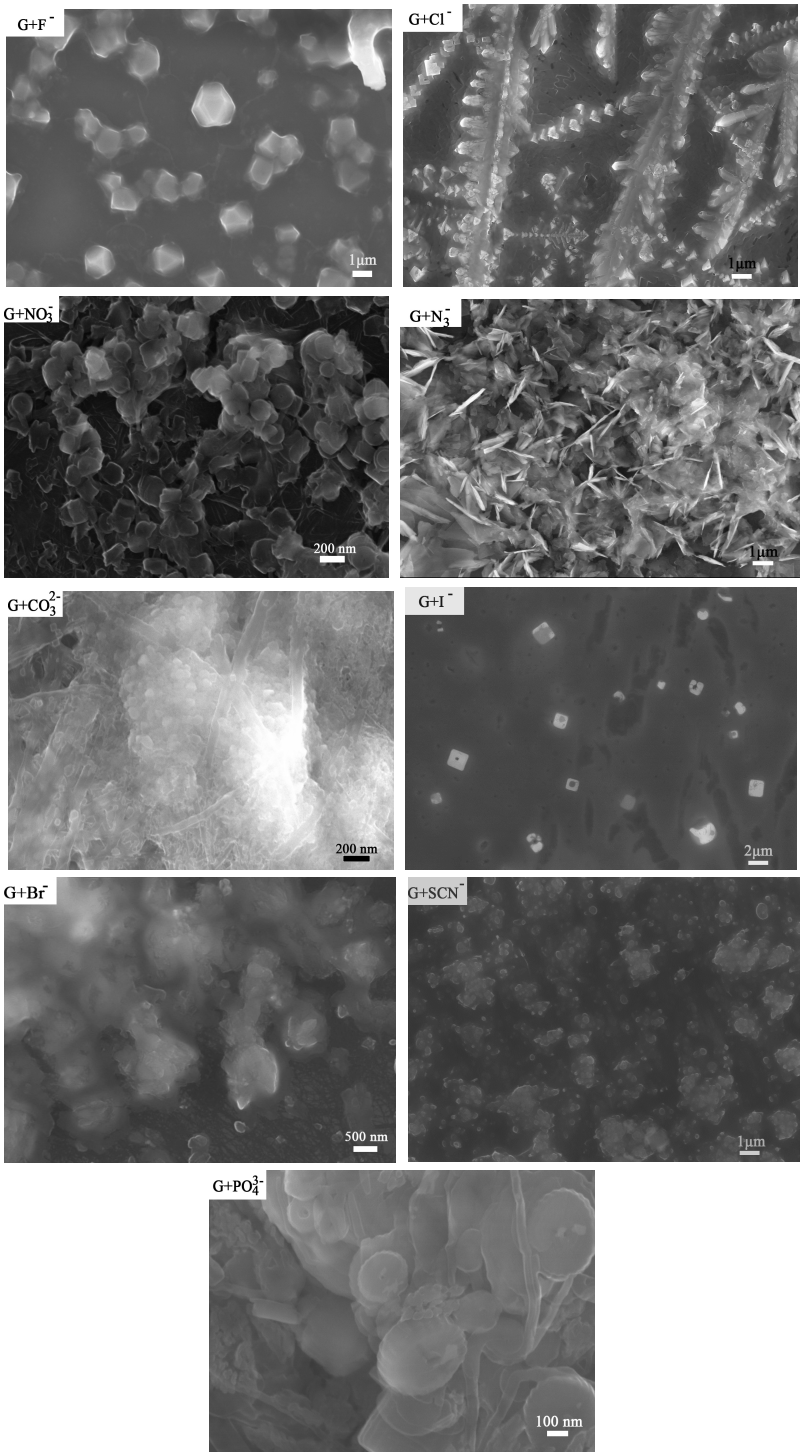


Fig. S9 SEM of MOGs after dipping in different anions. The concentration of the anions is 0.03M, respectively.